

THE OZONE HOLE

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Preamble

The original module on 'Ozone Hole' was produced in 1992 under a Project entitled 'Development of Material in Chemistry on Some Current Topics of Human Concern' of the Department of Education in Science and Mathematics (DESM) of the National Council of Educational Research and Training (NCERT). In the last decade, the phenomenon of Ozone Hole has gained much importance for human kind in general and scientists in particular. Studies concerning the phenomenon has led to a Nobel Prize in 1995 – shared jointly by Sherwood Rowland, Mario Molina and Paul Crutzen.

A decade later, this module is being revised and wherever possible new data and information added.

June 2004

FOREWORD

The day to day relevance of Chemistry to the critical issues facing the human kind do not often get highlighted substantially in Chemistry textbooks themselves because of several constraints connected with textbook development. Thus, with the objective of generating greater awareness of the role of Chemistry in such critical issues, the Department of Education in Science and Mathematics (DESM) of the National Council of Educational Research and Training (NCERT) has undertaken a project of "Development of Material in Chemistry on Some Current Topics of Human Concern" Under this project, it is proposed to develop booklets/ modules on selected topics for teachers and students of senior secondary classes. The booklets could be of interest to all others who wish to know about these topics. The present booklet is the first product of this Project.

The theme of depletion of Ozone layer is of topical interest in view of human kind's concern for environment. This booklet scans through the subject briefly but touches upon all major aspects of 'Ozone hole' - elementary properties of this oxygen allotrope, mechanisms attempted to explain Ozone depletion in particular, the chemical aspects of the reactivity of the chlorofluorocarbons, and the contributions of national and international agencies towards the understanding and rectification of the problem.

The material in the booklet has been developed by Prof M Chandra of the DESM. The original manuscript was reviewed by Prof. B.L. Khandewal, Department of Chemistry, I.I.T Delhi, Dr Sushmita Chowdhary, Gargi College, New Delhi; Dr. A.K Kaushal, Principal, Army School, Delhi Cant and Shri P.S. Shankar (Rtd.) Editor, J S.I.R. The NCERT is thankful to them. We would welcome Comments which can lead to the improvement of this effort.

November, 1992

A.K Sharma
Joint Director, N C E R T

ACKNOWLEDGEMENT

I am grateful to Prof. A.K. Sharma, Joint Director, NCERT for sparing some of his valuable time for going through the manuscript and for agreeing to write the foreword. My thanks are to Prof. K.V Rao, Head, DESM, Prof. A.K. Misra, Dean (Academic), Prof. Kuldip Kumar, Head, PPMED for their support. My thanks are to Prof. B.L.Khandelwal, I.I.T Delhi; Dr. Sushmita Chowdhury, Gargi College, New Delhi; Dr. A.K. Kaushal, Principal, Army School, Delhi Cant and Shri P.S. Shankar (Rtd) Editor, J.S.I.R., for their critical comments on the first draft of the material.

Last but not the least I am thankful to Smt. Annie Aphren for very ably typing the first draft and the final manuscript and the administrative staff of the DESM who have rendered help to me, whenever needed, for successful completion of this project.

M Chandra
Professor, D E S M
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October 1992

Life on earth is dependent on Ozone, almost as much as it is dependent on oxygen and water. Thus, depletion of the Ozone layer as a result of human activities and natural calamities is a major threat to humanity. According to the United Nations Environmental Programme (UNEP), overall Ozone level has not yet dropped, but measurements made during the Antarctic Spring have shown that levels have fallen by 40% in just a few years creating a "hole" in the Ozone veil. If proper precautions are not taken now, the thinning of this Ozone layer can influence the well being of the entire humankind - since depletion of the Ozone layer will let in more of the sun's ultraviolet radiation, which will damage agricultural yield, the ocean eco system, and will result in a rise in incidence of skin cancer and eye diseases.

The Indian Government fully shares the international concern on depletion of Ozone layer, and participates in the global effort to save this depletion. India had been an active participant in the (March-85) Vienna convention on "Protection of the Ozone layer", and along with other developing countries, India had sought and obtained amendments in the (Sept '87) Montreal Protocol on "Substances that Deplete the Ozone Layer". In fact the Indian Minister of State for Environment had been unanimously elected the President of the Fourth Conference of Parties (COP) of the Montreal Protocol held in Copenhagen, Denmark in 1994. This election was a clear indication of India's leadership role in the global environmental fora in general and her concern in the phenomenon of Ozone depletion in particular.

An understanding of the phenomenon of Ozone depletion, "Ozone hole" and the steps that are being taken by the international community - of which India is a part, should be useful for our student and teachers. With the hope of providing such information to students - who are the future of this country and the teachers who help to create this future, this booklet on Ozone depletion and consequences has been developed under the DESM's Project "Development of Material in Chemistry on Some Current Topics of Human Concern".

The booklet "The Ozone Hole", is based on information available in national and international scientific journals and books. The booklet has been developed basically in three parts: the first part deals with topics such as Ozone and its properties, importance of Ozone for the survival on earth and the so called "Ozone hole". The second part briefly mentions the various theories that have been proposed from time to time to explain the depletion of the

Ozone layer - the current acceptable theory being the "chlorofluorocarbon theory". In the last section a brief mention has been made to the steps that are being taken internationally (India included) to prevent further depletion of the Ozone layer. A detailed reference of the literature cited in the text appears at the end of the booklet, which may help those, who are interested to know more about the phenomenon.

Ozone, O_3 is the triatomic allotrope of oxygen. It is an atmospheric trace gas, but instead of being found in a constant fractional abundance in the atmosphere, concentration of Ozone is very sharply dependent on altitude, most of the Ozone being pictured as contained in an Ozone layer about 20 km thick, condensed at an altitude of about 20 to 30 km, i.e. in the stratosphere. The Ozone layer is not uniform around the world, it varies in density, being least dense over the equator and most dense over high altitude. The Ozone layer also changes through the year and is best developed over polar regions in early spring.

Ozone is an unstable, blue diamagnetic gas at room temperature and pressure, with a characteristic "fishy" smell. It can be detected by its smell in concentrations as low as 0.01 ppm. Ozone condenses to a deep blue liquid (b.p. 161 K) and to a violet-black solid (m.p. 80.5 K). Both the liquid and the solid are explosive due to decomposition into gaseous oxygen.

Being an "oxidising air pollutant" or a so called "oxidant" – that is, a member of that group of compounds in the air which are of highly oxidising nature, Ozone is a hazard in the ground level for living beings, maximum permissible concentration for continuous exposure being 0.1 ppm. It damages leaves, decreases yield and growth of agricultural plants and causes serious damage to textiles and elastomers (e.g. causes cracks in rubber tyres). In animals and plants it primarily attacks the lungs and the respiratory tract, but changes have also been observed in the hearts and brains of animals. (1)

However, in spite of the above, there are certain properties of Ozone which make it crucial on earth. One outstanding feature of ozone is the relationship between the absorption spectrum of ozone and the protection of the living systems from UV-B radiation*

Macromolecules, such as proteins and nucleic acids that are characteristics of living cells, are damaged by radiations of wave length less than about 290×10^{-9} m. Major components of the atmosphere, especially oxygen filters out solar UV radiation with wavelength less than 230×10^{-9} m (at that wavelength only about one part in 10 of the

* The UV spectrum can be divided according to the wavelength as UV-A, UV-B and UV-C which covers wavelengths 320 to 400×10^{-9} m, 280 to 320×10^{-9} m and 200 to 280×10^{-9} m respectively

intensity of an overhead sun would be transmitted to the earth), but at wavelengths greater than 230×10^{-9} m, the only species in the atmosphere capable of absorbing the sun's radiation is ozone. Ozone has an unusually strong absorption just at the critical wavelength ($230 - 290 \times 10^{-9}$ m), so that it is an effective filter for UV-B radiation, in spite of its relatively small concentration. (2)

Excess of UV radiation on reaching the surface of the earth affects the growth and reproduction of phytoplankton (small plants that constitute the base of the oceanic food chain, manufacturing materials that sustain virtually other organisms in the marine ecosystem), and could cause changes in human skin and eye leading to skin cancer and cataract. It would also affect the immune system

Sensitivity of plants in terrestrial ecosystems to UV-B radiation has not yet been comprehensively studied, however, half of the plants, including some important agricultural crops tested, are found to be sensitive to UV-B radiation. According to one estimate, a 10 per cent reduction in O_3 would correspond to a 100 per cent increase in DNA damaging UV-B radiation reaching the earth. (3)

The Ozone balance

The ozone concentration in the atmosphere is influenced by a dynamic balance between many physical and chemical formation and breakdown processes. Ozone is formed and destroyed at all altitudes of the atmosphere, as well as in the troposphere (up to 10 km above the surface of the earth) and in the stratosphere. The effects of the formation and destruction of ozone vary at different altitudes. The total ozone concentration added up over all altitudes, i.e. 'total ozone', is the determining factor for the absorption of UV-B radiation. Changes in the vertical ozone profile are also important for potential climate changes, since a decrease in ozone in the stratosphere allows more UV radiation to reach the earth's surface which allows increase in the phenomenon of 'global warming'. (4) Shift in the vertical ozone profile can cause changes even if the 'total ozone' remains unchanged.

Table 1a
EFFECT OF OZONE ON HUMAN HEALTH

| Effect | Conc. (ppm) | Exposure |
|---------------------------------------|-------------|----------|
| Increased airway resistance | 0.1 - 1.0 | 1 hour |
| Extreme fatigue, lack of coordination | 1.0 - 3.0 | 2 hours |
| Severe cough | 2.0 | 2 hours |
| Pulmonary edema | 9.0 | Unknown |

Table 1b
OZONE LEVELS IN INDIAN CITIES

| City | Range of average conc. (ppm) | Range of max. conc. (ppm) |
|----------|------------------------------|---------------------------|
| Bombay | 0.003 - 0.017 | 0.026 - 0.047 |
| Delhi | 0.006 - 0.013 | 0.012 - 0.028 |
| Calcutta | 0.013 - 0.018 | 0.023 - 0.078 |
| Kanpur | 0.020 - 0.100 | 0.028 - 0.135 |

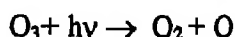
Source Based on: RAO (C S), Environmental Pollution Control Engineering, Wiley Eastern Ltd. (1991) 67.

The main formation and destruction mechanism of ozone is triggered by UV radiation. Ozone is formed in the stratosphere where oxygen molecules absorb U V-C radiation.

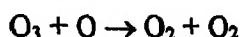


(M is a third particle acting as a collision partner)

Ozone itself is further photo dissociated by radiation of other wavelength (visible and longer wavelength UV radiation).



The resulting O can in turn breakdown O_3 .



However, this ozone breakdown mechanism is insufficient to explain either the natural ozone concentration or change in its concentration. This was one of the issues, the investigation of which led the scientists to the phenomenon that is now popularly known as the "Ozone hole" (5).

What is this ozone hole?

During the past century, periodic appearance of "stratospheric clouds" has been recorded over both the pole at an altitude of about 20 km. These clouds, which extend 10 to 100 km in length and are several km in thickness, glow as seashells do, and are therefore termed as nacreous clouds meaning mother of pearl. Two other types of clouds are also observed, those consisting of nitric acid instead of pure water, and the third type - identical to nacreous clouds in chemical composition but formed in a process that results in larger clouds with no 'glow'. These three types of clouds formed over the poles are referred to by the scientists as polar stratospheric clouds, or PSC-s. Recent work indicates that in the Antarctic atmosphere, the PSC-s trigger ozone depletion, and in the Antarctic atmosphere, they help create the 'ozone hole' - which is actually not a hole, but is a region that contains an unusually low concentration of ozone (6).

Although the ozone hole over the Antarctic is remotely located, but since shifting circulation patterns carry masses of ozone depleted air northwards, the 'Ozone Hole' can lead to widespread ozone depletion through the stratosphere - and thus is a cause for concern.

It was in 1985 that Joseph Ferman and his coworkers at the British Antarctic Survey first reported that significant ozone depletion had been occurring over the Antarctic. Since late 1970s, satellite measurements have shown that about 70 per cent of the ozone over the Antarctic is lost during September and October, at an altitude of 12 to 30 km above the surface of the earth. However, the protective Ozone layer is now found to be disappearing faster than previously thought. According to a NASA (National Aeronautical and Space Administration of USA) data, depletion of 4 to 5 per cent has occurred since 1978 over the USA, though past studies have indicated half that amount. Besides the larger than expected drop, ozone depletion has been found well into the spring months, whereas researchers have previously believed the phenomenon to be significant only in winter. (7)

Data based on measurement by the TOMS (Total Ozone Mass Spectrometer) of the NIMBUS 7 satellite over about 12 years upto May 1990 showed that, between 65° N and 65° S, the ozone column abundance has decreased on the average by 3 per cent over the whole period. But the trend is not geographically uniform, the variation being extremely small and not significant near the equator. Statistically significant depletion becomes apparent in both hemispheres pole wards of 30°. The reduction in the ozone column is particularly large (3% per year on the average) near the Antarctic continent especially in spring, and even at 60° S, a near trend of -0.6 per cent per year is reported. These large perturbations are clearly associated with the formation of the "Antarctic Ozone Hole". An important but poorly understood phenomenon is how the ozone poor air from the polar region is mixed into lower latitude in late spring (November). When the polar vortex (the 'home' of the hole) breaks down. In the northern hemisphere the largest depletion appears to have taken place at mid latitude - the average depletion being 0.4 to 0.5 per cent per year in the belt of 40 - 50° N with trend of - 0.2 per cent per year in summer and - 0.6 per cent per year in winter. (8)

Ozone depletion in the Arctic

The polar vortex -i.e. stream of air that centres at the poles in winter time isolating the air within, are found in the winters both at the Antarctic and the Arctic. However, milder winters and thus fewer stratospheric clouds at the north pole have so far saved the Arctic from the massive ozone depletion that occurs only in the Antarctic. Although at first glance the two regions appear to be similar: very cold and dark winters, cool with long daylight in summer covered by ice and snow - the Arctic and the Antarctic are, in fact, very different - meteorologically, biologically and geographically. The south pole region is an ice covered continent surrounded by ocean, whereas the north polar region is an ice covered ocean surrounded by continents. Perhaps the more important differences between the two poles concern the longevity of the polar vortex - the ring of rapidly circulating air that confines the ozone depletion. In the Antarctic, the vortex remains intact throughout the polar winter, well into midspring. Ozone destruction begins in September with the return of sunlight. Loss of ozone reaches its peak in October. In the Arctic, where circulation pattern differs significantly from that in the Antarctic, the vortex disintegrates by the time polar spring (March-April) arrives. A feedback mechanism may further extend the lifetime of the Antarctic vortex. Ozone absorbs sunlight, thus heating the atmosphere; depleted ozone level causes the air to remain cold longer. Such cold air encourages the formation of PSCs and stabilizes the vortex. Measurements have shown that the temperature inside the vortex has declined over the past decade and the duration that the vortex remains intact has increased. It is observed that the PSCs form more frequently as the temperature drops, completing the positive reinforcement of the system. The early breakup of the Arctic vortex makes it difficult to assess the magnitude of the ozone loss in the northern hemisphere.

It is found that Arctic stratosphere above 18 km suffered ozone depletion equivalent to 8 per cent of the total amount of ozone over the Arctic. For comparison, total ozone loss over the Antarctic averages above 50 per cent or more. Thus, though conditions exist in the Arctic that facilitate the formation of the ozone hole, yet, unless the Arctic temperature drops significantly, the extent of ozone depletion in the Arctic should never compare with the loss in the Antarctic. A lower average winter temperature in the Antarctic would enable PSCs to form over a region of greater altitude and to persist longer.

Because the ozone hole requires the presence of polar stratospheric clouds and a stable vortex for its creation, it is necessarily trapped near the poles, where few people live. But this does not imply that loss of ozone is restricted to Polar Regions. As the Antarctic vortex breaks up, pools of ozone poor air spread over the southern hemisphere creating a small average ozone loss across the hemisphere. It is suggested that the Antarctic vortex may act as a chemical processor. Ozone rich air may be entering the vortex and ozone poor air may be transported outward to the rest of the hemisphere.

Theories of ozone depletion

Scientists have proposed many theories explaining the causes of the 'Ozone hole', viz the Dynamic theory (9), theory relating to events external to the earth (10), chemical reasons leading to ozone depletion, etc. However, the chemical interpretation relating to "halogen free radicals" to global ozone loss has now emerged as the theory to explain the "depletion observations". This theory suggests that chlorine compounds might be responsible for the "ozone hole". Chlorine, it is claimed, primarily enters the atmosphere as a component of chlorofluorocarbons (CFCs), produced due to human activities (11).

Chlorofluorocarbon (CFCs)

The general term CFC refers to a group of compounds, which are derived either from open chain (aliphatic) or closed ring type (alicyclic) hydrocarbons where the H atoms are completely or partially replaced by fluorine or chlorine. Some CFC molecules also contain bromine. These are commonly called "halons" and are used exclusively as fire extinguishers. When all the hydrogen atoms of the hydrocarbon are replaced by a combination of fluorine and chlorine or bromine, a "fully halogenated" compound results.

The first CFC, R-21 (dichloromonofluoromethane), was developed in 1928 as an alternative to coolant gases used in refrigerators. Soon several CFCs were developed by chemically reacting halogens (fluorine, chlorine and bromine) with molecules of simple hydrocarbons, where in the hydrogen atoms in a hydrocarbon molecule are replaced with fluorine and either chlorine or bromine. Being stable, nontoxic, non-inflammable, non-corrosive, the CFCs are used in industries as blowing agents for foams, plastics, as aerosol propellants, solvents for cleaning precision electronic equipment besides as refrigerants. (12)

Table 2
Some Commonly used CFCs

| Substance | Chemical formula | Application |
|-----------|------------------------------|--|
| R - 11 | CCl_3F | Refrigeration, aerosol, foam blowing, solvent, etc |
| R - 12 | CCl_2F_2 | Do |
| R - 22 | CHCl_2F | Do |
| R - 113 | $\text{CCl}_2\text{FCClF}_2$ | Aerosol, foam blowing, etc |
| R - 114 | $\text{CClF}_2\text{CClF}_2$ | Refrigeration, aerosols, foam blowing |
| R - 115 | CClF_2CF_3 | Refrigeration |

Source. TIDE 1 (1991) 29

In India we have a total licensed capacity for CFC production of over 20,000 metric tonnes/year. However, the actual production is about 25% of this capacity. We do not have production facilities for halons, and meet its requirement by importing these substances to the tune of 300 metric tonnes/year. 10% of the CFCs in India are used in aerosol, 5% in blowing, 83% in air conditioning and refrigeration and 2% in other activities (13)

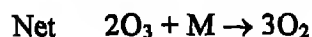
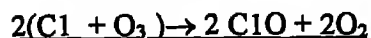
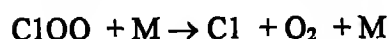
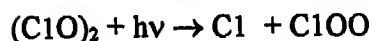
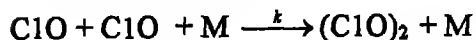
The chlorofluorocarbon (CFC) –PSC theory of ozone depletion

Over the decades, through vertical transfer, these inert CFCs eventually reach the middle stratosphere, above 30 km or higher from the earth's surface. Here, the UV radiation from the sun tears them apart. The resulting chlorine exists either as chlorine monoxide (ClO), formed as a reaction product with ozone or as free chlorine. Gases in the atmosphere such as NO_2 or CH_4 react with ClO or chlorine, and trap the chlorine in inert chemical reservoir of chlorine nitrate (ClONO_2) and hydrochloric acid (HCl).

Chlorine reservoirs themselves do not destroy the ozone layer. In these compounds, chlorine remains inert and cannot react with ozone. Evidently, some mechanism in the Antarctic stratosphere frees the chlorine from these inert reservoirs. In 1986, it was suggested that it is the polar PSCs that initiate chemical reactions that free molecular chlorine from the reservoir.

These mechanisms have been proposed at different stages by different groups of scientists the net "ozone depletion" reaction remaining the same as $2\text{O}_3 \rightarrow 3\text{O}_2$

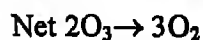
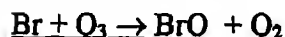
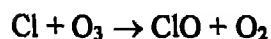
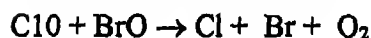
Mechanism I The mechanism suggested by M.J. Molina states that ClO dimer is involved in a quartet of reactions



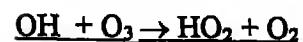
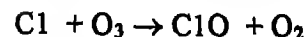
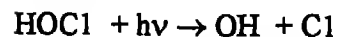
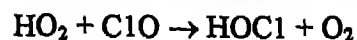
Here $h\nu$ represents the UV photon, "M" is a collision particle (either N_2 or O_2) and k is the rate constant of the rate limiting step

Mechanism II: The active chlorine freed by the PSCs also plays a role in another significant catalytic process - one that involves bromine. Human activities contribute bromine to the atmosphere, bromine being an important component of halons (used as fire extinguishing compounds) the reaction may account for 20% of ozone destruction. Bromine reacts with ozone forming bromine monoxide (BrO). This reacts with chlorine monoxide (ClO) forming molecular oxygen and freeing bromine and chlorine atoms, which then react with ozone.

The process gets repeated



Mechanism III: A third mechanism, suggested by Solomon and coworkers proposed that chlorine and hydrogen radicals are coupled in the following sequence.



Many other theories have also been proposed, but have not gained support.

The current PSC - chlorofluorocarbon theory for the formation of the "ozone hole" explains many observations. The release of CFCs from human activities, mainly in the northern hemisphere, is responsible for depletion of ozone in the southern hemisphere, because the long atmospheric lifetime of CFCs causes them to be uniformly distributed throughout the atmosphere. The "ozone hole" occurs near the Antarctic during spring months, because the formation of the hole requires the presence of stratospheric clouds, which form only during the coldest time of the year. The first rays of spring sunlight initiate the chemical reaction that depletes ozone. The first concerned experimental effort to evaluate these theories was the American National Science Foundation supported Ozone Experimental Expedition (NOZE -1) (14)

However, this "chlorofluorocarbon theory" had been disputed by two scientists – Rogelio Maduro and Ralf Schauerhammer. In their book "Holes in the Ozone Scare" (21st century Science and Technology Publishers, 1992) they claimed that natural sources of chlorine e.g , chlorine vented into the atmosphere by evaporating seawater and by volcanoes far exceed the chlorine from CFCs. Mount Erebus on Antarctica, they claim, alone ejects 1000 tonnes of chlorine a day, annually venting 50 times more chlorine than an entire year's CFC equivalent. They also claim that CFCs are degraded by micro organisms on the ground and in the soil and a large amount of CFCs are also absorbed in the ocean despite their low water solubility. The two scientists refuted the widely held assumption that CFCs rise in the air and climb all the way to the stratosphere and destroy the ozone layer

Studies also report that the burning of savannas, forests and fire wood emits substantial quantities of methylchloride (chloromethane) that contributes to the depletion of the ozone layer as well. According to this study, methylchloride is more significant, than some of the industrial compounds such as CFCs as far as the developing countries are concerned. The study points out that while methylchloride contributes only about 5% to ozone depletion emission globally, it contributes about 40% of ozone depletion accumulations in countries such as China, India, tropical Africa and Brazil. Certain types of common tropical plants emit methylchloride in the range of 0.1 to 3.7 microgram /dry leaf / hour. However, there remains a substantial shortfall in overall methylchloride budget.

Although methylchloride is the largest ozone depleting chlorine compound, but with continuing tropical deforestation, natural source of chlorine compound may decrease (15). In comparison, CFC used as refrigerant makes up to 26% of ozone depletion emission in these countries. However, the status of, methylchloride in the atmosphere is still marked with uncertainty and the amount of methylchloride, resulting from natural and man made sources is not well defined. (16)

Methylbromide (bromomethane) - a highly toxic gas used for range of purposes, including the sterilization of soil in greenhouses, appears to be outstandingly effective at destroying the earth's ozone layer as well. According to scientific assessment from the United Nations Environmental Programme (UNEP) bromine derived for methylbromide is 30 to 60 times more efficient than chlorine at destroying ozone. Model calculations indicate that main emission of methylbromide may have accounted for upto 10% of the current global loss of stratospheric ozone. However, only quarter of the earth's emission of methylbromide comes from manmade sources, algae in the sea have been making this for millenia. A recent re-evaluation has shown that high ozone depletion potential of bromine in polar and middle latitudes has been overlooked. Bromine also appears to act faster when chlorine is present. Since the UNEP report of June'92, the world has been faced with a problem potentially even more difficult than it faces in phasing out CFCs, halons, methylchloroform, methylchloride, carbontetrachloride. The question is, how to stop using a chemical with which the world's food trade is highly connected and whose use many countries specify as quarantine measure? Methylbromide is described by users as an unique chemical, able to kill everything from nematodes in soil to fungus in vines and from rats in airline cargo holes to weevils in wheat. It has been in widespread use for at least thirty years. Since it is highly toxic in short term, expensive safety protections are essential. (The users must wear a respirator)

Of the 60,000 tonnes of methylbromide used worldwide each year, 80% go to sterilise the soil so that crops may be grown continuously under glass. The other 20% find a wide range of application: quarantine purposes, fumigating ships and containers, art collection, and stored commodities such as rice, coffee, tea, nuts, spices, dried fruits, fish meat and potatoes. Many developing countries are dependent on the fumigation of products before export. With so many people relying on methylbromide for food, can its application be limited? (17)

Ozone depletion due to volcanic eruption

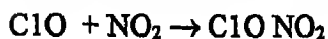
Natural causes such as volcanic eruptions also contribute to depletion of the Ozone layer. It has been found that, for a period of up to two years after major volcanic eruptions, the atmospheric concentration of sulphuric acid aerosol* in the stratospheric eruption cloud may be comparable to those of nitric acid aerosols, and this might also play a part in atmospheric heterogeneous chemistry

Based on laboratory studies and calculations, the AASE II (Airborne Arctic Stratospheric Expeditions) scientists confirmed a hypothesis that reactions in sulphate aerosols are siphoning off oxides of nitrogen - that family of reactive nitrogen compounds which place a brake on ozone depletion, by tying up reactive chlorine and bromine as less reactive nitrates.

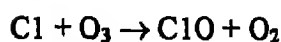
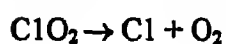
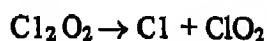
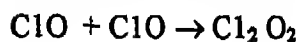
These reactions on sulphate aerosol using up nitrogen oxide are as follows:



The above reactions block the reaction that ties up chlorine oxide viz



and thus accelerate ozone loss according to the chlorine monoxide dimmer mechanism (as stated in Mechanism I), i.e.



Though Ozone loss caused by sulphate aerosol is of lower magnitude than that caused by the PSCs, but the involvement of sulphate aerosol in accelerating ozone loss has significance all

* Aerosols are colloidal systems in which liquid or sometimes solid particles with diameter measuring about 10^{-1} mm to 10^{-6} mm are distributed in a gas phase (such as air). Such two-phase distributions can be artificially produced by aerosol products

over the globe, not just at the poles. The stratosphere holds a permanent thin veil of H_2SO_4 droplets, which has increased in the recent past because of many reasons including volcanic eruptions, e.g. the El Chichon eruption of 1982 and the June 1992 eruption of Mt. Pinatubo in the Philippines.

Expedition scientists have found that as far South and the mid Caribbean, there are low concentrations of nitrogenoxides - due to reactions of sulphate aerosol particles and correspondingly elevated levels of chlorine monoxide and bromine monoxide. They concluded that these relatively high levels of active halogen explain the subtle loss of ozone that has taken place since the early 1980s, over the mid-latitudes. Though less dramatic than the 'Antarctic ozone hole', with at worst a 10 per cent loss of ozone over the past 10 years, this depletion extends - over wide areas of the globe and persists from winter into early summer (18)

In fact, if there is no substantial reduction on in the CFC emission, the impact of future volcanic eruption clouds on ozone may be quite severe, specially since the clouds have a typical lifespan of, 1-2 years, and may cover larger parts of the earth including the equatorial region, where the unperturbed ozone column is already relatively small (19).

Efforts taken for the protection of the ozone layer

The solution to the problem of depletion of ozone layer needs a concerted effort of both scientists and politicians of all concerned nations. The solution, as it appears now, rests on regulating the release of CFCs to the atmosphere. The first stage towards such a regulation was reached with the UN convention on "Protection of the stratosphere" adopted in Vienna in March 1985. Subsequently, in September 1987, about 40 countries of the world signed at Montreal Canada, the "Protocol on Substances that Deplete the Ozone Layer", popularly known now as the "Montreal Protocol". On June 19, 1992 India also signed the Montreal Protocol. This protocol outlined a procedure for restriction by 1990, of global emission of CFCs to 50% of the 1986 levels, with provision for reviewing the restrictions every 4 years. This reduction however, would have allowed atmospheric levels of chlorine to increase to twice the current levels by the end of the century. As scientists have become more certain of

the chemistry of ozone depletion, and the role that chlorine plays, swifter action was called for.

Thus, at two meetings - one at Helsinki in 1989 and the other, at London in 1990 the participating countries focused on efforts to phase out CFCs and on developing CFC substitutes. "The Asia Pacific Seminar on the Protection of Ozone Layer", held in January 1989 in Tokyo, aimed at reviewing and updating the existing scientific knowledge, and relevant information on ozone depletion and CFC Chemicals and provided a forum for an exchange of views among countries of the region. (20)

The London Amendments of the "Montreal Protocol" ratified by countries including India, came into force in August 1992. The amendment had set out a timetable for the reduction and phase out by the year 2000 of 11 ozone-depleting substances in addition to eight which were already covered by the protocol. It also required phasing out of methyl chloroform (1,1,1 trichloroethane) by year 2005. The London Amendment established a financial mechanism which included a multilateral fund to meet the incremental costs developing countries must incur in order to comply with the protocol. It also provided for environmentally safe substitutes and related technologies to be transferred to developing countries under fair favourable conditions.

The June 1992 UN Conference: "UNCED-92" (United Nations Conference on Environment and Development 1992) held at Rio de Janeiro, commonly known as the "Rio Conference" or the "Earth Summit", also addressed itself to the issues relating to depletion of ozone layer and its consequences (21)

As a consequence of the awareness about the 'Ozone Hole' and under the influence of the 'Montreal Protocol', researchers world over have now started to produce encouraging data showing an improvement in the ozone hole. Experiments conducted by Indian scientists at 'Maitri' - the Indian Antarctic Research Centre, during the year 1997-2002 showed that the 'Ozone Hole' in the year 2002 was not as deep as it was in 1997. The observation also showed an early recovery of the ozone hole in the year 2002 compared to 1997. Although the ozone hole data for the year 2002 does not by itself give any indication of the long term trend, but measurement show that the CFC concentration in the stratosphere is leveling off and at the lowest layer of the atmosphere, i.e the troposphere, CFC concentration has started

to decline due to the decision taken by the international community under the 'Montreal Protocol'. These measurements by the Indian scientists indicate that the ozone hole may soon start to improve, although this improvement will come slowly (22)

Alternatives to CFC

The high stability of the fully halogenated CFCs that make them so useful is the same characteristic that renders them dangerous to the stratospheric ozone layer. Because of their inert nature, the CFC molecules that are emitted in the lower atmosphere eventually diffuse into the stratosphere. The intense UV radiation there liberates chlorine atoms that then lead to reactions destroying ozone molecules.

Since there exists all over the world an enormously large number of equipment that use CFCs it is simply not possible to scrap all such equipment and install new ones. Thus, scientists have to find something that comes close to the existing compounds that are being used. Hence the key to developing CFC alternatives is to match the physical properties of the CFCs that are being replaced.

One way of doing this is to add hydrogen atom to the CFCs so as to ensure that the compounds are oxidised before they reach the stratosphere, and at the same time, have a close match in physical properties with those of the CFCs. If one replaces the Cl in CFC - 11 (CCl_3F) with hydrogen, the boiling point of the compound produced turn out to be far too low. Thus, one has to make the molecule heavier by going to a 2-carbon molecule. Working with 2-carbon fragments however, adds to the complexity of dealing with isomers. Also, there may be a wide variety of reaction routes involving a number of possible materials for obtaining the desired replacement compound. Each of these routes will have different problems associated with it, and each route has to be explored, if the best process is to be found. E.g. HFC - 134a ($\text{CF}_3\text{CH}_2\text{F}$) - which is a "partially halogenated" CFC, and therefore "less ozone depleting" material than a fully halogenated CFC such as CFC - 11 (CCl_3F), can be prepared from $\text{CCl}_2=\text{CCl}_2$ or from $\text{CHCl}=\text{CCl}_2$. A number of reactions take place as one adds fluorine and goes through various intermediates. Separating these materials leads to difficulties from the point of view of process development.

The "partially halogenated compounds", i.e., the HCFCs and HFCs are less stable in lower atmosphere, which is why they are acceptable as substitutes, but they are also less stable on catalyst surface. This also poses problems in the developmental efforts. (23)

Five such hydrofluorocarbons (HCFCs) have been developed and are now widely used. But some of the HCFCs eyed as substitute for CFC-11, attack the varnish on motor windings and some are also inflammable.

Presently the most desirable alternative compound to CFCs are taken to be those that contain no chlorine at all, only C, H and F. Such hydrofluorocarbons (HFCs) have no potential to deplete stratospheric ozone. Three such HFCs have been developed in limited quantities so far.

Other problems faced in the search for CFC substitutes are: high cost of chemical substitution and associated replacement technologies; lower energy efficiency of the CFC replacements; their toxicity and their potential to contribute to "green house effect."

Nearly 60 per cent of all CFC usage is energy related. Of this, two-third is as refrigerants, and one-third as blowing agents in foam insulation products. Small capacity refrigerators and freezers, including all such home appliances rely solely on CFC-12 (CCl_2F_2). In commercial air conditioning larger quantities of controlled compounds are used singly or in blends, which contain controlled compounds. Thermal significance of CFCs used in insulating foam were more widely appreciated following the energy crisis of the 1970s. An U.S. study had concluded that energy consumption impacts of using substitutes for blowing materials would cause a substantial increase in energy use. For most cases the cutback also implies increasing demand for electricity.

One of the important properties of the CFCs is their low toxicity. In fact, it is this property, along with their high stability and inertness, that had made the CFCs such sought after chemicals a few decades back. Though toxicity data on CFC substitutes are still inadequate, the higher toxicity of the CFC substitutes is posing problems in their effective use. Long-term toxicity tests are still required before the products can be manufactured commercially.

In addition to the problems related to the chemical and physical properties of the CFC substitutes, switching over to ozone benign technologies is very expensive. This is because of

high cost of substitution, Research and Development (R & D) costs and costs related to redesign of equipment. Developing countries such as India believe that their economies will find it difficult to bear this high cost.

Apart from their ozone depleting properties, the CFCs have been identified also for their 'greenhouse effect'. Molecule for molecule, the CFCs are 10,000 times more efficient in absorbing Infra Red (I.R.) radiation from the sun's rays than CO₂, making the CFCs the so-called 'greenhouse gases', gases which allow solar radiation to pass through the earth's atmosphere, but limit the energy that can later be re-radiated into space. Thus CFCs not only tend to have high ozone depleting potential, but because of their 'greenhouse effect' they also have high global warming potential. The CFCs are believed to account for about one-fifth of the perceived warming that has been attributed so far to atmospheric pollution. Now there are reports that HCFCs and even HFCs, may also have significant potential to contribute to greenhouse warming.(24)

One substance that could represent a fallback option as a refrigerant in the event of a broad ban on CFCs as well as HCFCs is propane. Although propane is inflammable, yet it is thermodynamically suitable for most electrically powered cooling appliances that now use CFC-12 or HCFC-22. Propane has low toxicity and would not require extensive testing in that respect.

Also, as less efficient CFC alternatives are identified and as redesigned equipment to use them reach the market, the higher installation and operating costs of these equipment could boost the economic competitiveness of alternatives to vapour compression cycles. The principal rival for commercial and industrial use is the gas-fired absorption chiller where cost performance has been improving as a result of several years of substantial Research and Development support.

In addition to the effects on energy use of CFC substitutes, utilities will also be directly affected by the somewhat later phase-out of halone fire extinguishers. The unique ability of halones to snuff out explosives without apparently leaving any residue has made them ideal as close quarters critical facility fire extinguishers on aircrafts, ships, in computer rooms and electric power facilities. Evolving satisfactory alternatives to halone fire extinguishers reportedly is proving to be more challenging than developing CFC substitutes.

Thus despite the world spotlights on the ozone issue, the outlook for future without CFCs remains clouded in uncertainty. (25)

One proposed solution to prevent the formation of the annual 'Ozone hole' over the Antarctic has been to inject ethane and propane gas each year into the stratosphere above that continent. The hydrocarbons could scavenge chlorine atoms, interrupting the chain reactions that lead ozone depletion. However, many scientific, technical, legal and ethical issues have to be sorted out, before trying such an experiment. All the injections have to be timed just right. If too late, the hydrocarbons would not have time to disperse through out the isolated mass of air above the Antarctic where the ozone hole forms, on the other hand, if the injection is done too soon, the gases could simply float away towards lower altitudes. (26)

Table 3**CFCs AND ALTERNATIVES**

| Use | Current CFC used | Alternatives |
|------------------|---|---|
| Refrigeration | CFC - 11 | Helium, ammonia, HFC-142b, HCFC-22 |
| Air conditioning | CFC - 11 | HCFC-22 + HCFC-14b, HFC-134a |
| Foam blowing | CFC - 11 | Water blown foam, HCFC-141b, HCFC- |
| | CFC - 12 | 22, HCFC-123, alternative insulation |
| Sterilization | CFC - 12 | CO ₂ , HCFC -22 |
| Fire suppression | Halons | CO ₂ , no known adequate substitute for same use |
| Solvents | CFC - 113 | Aqueous cleaning, terpenes, no clear technologies |
| Aerosols | CFC - 11 | CO ₂ , N ₂ O |
| | CFC - 12 | Pump spray |
| Source: | Makhijani A and Bickel A. Protecting the Ozone layer. Energy Environment Monitor 6 (1990) 7 | |

The Indian Scene

To meet the country's commitment to ozone depleting substances (ODS) phase out under the 'Montreal Protocol', and to disseminate information on ozone and ODS, the Ministry of Environment and Forest of the Government of India has established an 'Ozone Cell'. In July 2002, the Ministry also registered a society namely 'Project Management Unit for Phase out of Ozone Depleting Substances (PMU)', to work under the 'Ozone Cell'. The society undertakes activities related to phase out of ozone depleting substances, and facilitates compliance with the provision of the Montreal Protocol. The technical assistance component for CFC production phase out is a subject under this society

The Ministry also provides customs and excise duty exemption to ODS phase out projects. Detailed guidelines and procedures have also been finalized to grant duty exemption to new investments with non ODS technologies. A ban has also been imposed on trade of ODS. Further, the ozone depleting substance (Regulation and Control) Rule 2000 has been notified to provide a legal framework for ensuring compliance of the Montreal Protocol. (27)

The Ministry of Environment and Forests had initiated a Research and Development (R & D) programme on various aspects of development of CFC substitutes. The outlay for this 5 year project had been 9.95 crore and was carried out in selected CSIR (Council of Scientific and Industrial Research) laboratories. The IICT (Indian Institute of Chemical Technology), Hyderabad is the focal laboratory for developing technology for CFC substitutes. Under this major project the laboratory was involved in developing technology for the production of HCF 134a -which is a comparatively safe substitute for CFC s used in air conditioning and refrigerator units

The other CSIR laboratories involved in this work are NCL (National Chemical Laboratory) Pune, working on development of CFC alternatives for air conditioning and refrigeration, ITRC (Indian Toxicological Research Centre) Lucknow, working on toxicological evaluation of CFC substitutes, IIP (Indian Institute of Petroleum) Dehradun, working on assessment and development of lubricants compatible with CFC substitutes. (28)

CFCs and HCFCs are being manufactured by five companies in India, most of them producing CFC-11, CFC-12 and HCFC-22. (29)

Concluding remarks

Ozone has existed in the upper atmosphere of earth ever since oxygen has been a component of the atmosphere. Qualitatively, the "earth's atmosphere will contain ozone as long as the sun shines. Quantitatively however, in view of natural calamities and potential man made perturbations, one can only speculate on the constancy of the stratospheric ozone concentration profile

Though at present, there is no ozone loss over India*, but the depletion of stratospheric ozone layer has become an important topic of discussion here

Over the past few years, there has been such extensive information about the threat to the ozone layer and the damage to humankind and the ecosystem which could result from this depletion, that stratospheric ozone has now grown from being a part of atmospheric science to an issue of moral concern of the public at large. This concern for ozone has been based not on the gas itself, but over its potential depletion and the biological and climatological effects, which might result from such depletion. Thus, the "ozone problem" has today become a part of the global inter-governmental negotiations - which includes even the mighty UN system

According to the leading climate researchers who had met at Buenos Aires in November 2000, the international effort to halt ozone depletion through legislated reduction of use of CFC has been a success. Researchers predict that polar ozone hole should close for good in about 50 years, i.e around 2050. But the complicated effect of greenhouse gases could lengthen the process. Although, there is still no direct evidence that the ozone layer is recovering, but the stabilizing of CFC concentration in the lower atmosphere means that such a recovery is assured. It is predicted that the CFC concentration will take another decade or so to level off, and begin to decrease - indeed, the biggest ozone hole was seen over the Antarctica in the year 2000. The reason for the time lag is that the CFC-s are inert and persist in the atmosphere for up to a century. This delay has infact led to some confusion about the effectiveness of the Montreal Protocol. Assuming that the current CFC policies continue, the forecast is that, ozone holes that open up over the Antarctica every year and over

* The ozone level in India is reported to vary between 350 Dobson units (1 Dobson unit is equal to 2.7×10^{10} ozone molecules/cm³ of air) compared to 1210-115 Dobson units recorded during the peak ozone hole periods (30)

the Arctic periodically should be gone by 2050.

However, higher concentration of greenhouse gases – the effect of which have not been reliably modeled – could push the date back by a few decades. Although the greenhouse gases warm the lower atmosphere, but they cool the stratosphere forming ice crystals which catalyze the destruction of ozone by CFC-s.

The combination of lingering CFC-s and more greenhouse gases could lead even more severe ozone holes in the short term,. Ozone could be in its lowest level even by 2005, but in the longer term, there will be a recovery. Large volcanic eruption which launch dust into the stratosphere, could also cause short term depletion of the ozone layer ((31)

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